Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 4 (2011) 23–28

Energy Procedia

www.elsevier.com/locate/procedia

GHGT-10

Degradation of aqueous methyldiethanolamine by temperature and oxygen cycling

Fred Closmann and Gary T. Rochelle*

Luminant Carbon Management Program, Department of Chemical Engineering, The University of Texas at Austin, 1 University Station C0400, Austin, Texas, 78712, USA

Abstract

The primary degradation products identified in aqueous 7 molal (m) methyldiethanolamine (MDEA) loaded to 0.1 mol CO_2/mol alkalinity and degraded in the Integrated Solvent Degradation Apparatus (ISDA) were diethanolamine (DEA), bicine and formate. DEA and bicine represented 43 and 9 % of the carbon loss, respectively, after the solvent was cycled for 167 hours. An MDEA loss of 8.8 mM/hr and a formate production of 0.6 mM/hr were measured when 7 m MDEA cycled from 55 to 120 °C in the ISDA in its initial design, which allowed bubble entrainment. When bubble entrainment was minimized through coalescence and removal, the MDEA loss and formate production were cut in half (4.6 mM/hr and 0.31 mM/hr). When dissolved oxygen was stripped from cycled MDEA with N_2 gas at 2 L/min, the MDEA loss was negligible, and the formate production was reduced to 0.05 mM/hr. Designers of CO_2 scrubbing systems for post-combustion capture should minimize dissolved and entrained oxygen carryover into the stripper. Stripping of entrained and dissolved oxygen before the stripper is recommended to avoid high temperature oxidation.

An oxygen solubility limit exists at a thermal reactor temperature of 120 °C which can be expressed as an apparent upper limit of dissolved O_2 available to degrade ~1.3 mM MDEA/pass. The oxidative degradation model compensates for the complete consumption of dissolved oxygen in the thermal reactor at higher temperatures (>100 °C). The model assumes that all oxidative degradation is occurring in the thermal reactor under plug-flow reactor (PFR) behavior, and compensates for complete oxygen consumption with a stoichiometric factor (S). The regressed values of S, E_a, and k_o for formate were 0.1, 107 kJ/mol, and 2.4 1/hr, respectively. The predicted rates of formate production approximately match the measured rates over the entire measured temperature range of 55 to 120 °C. Oxidation Inhibitor A is ineffective over the temperature range of 90 to 120 °C in cycled solvents.

methyldiethanolamine; piperazine; oxidative degradation, solvent cycling; diethanolamine

1. Introduction

Alkanolamine solvents including aqueous MDEA have been used for decades for acid gas treating where feed gas composition is typically 75 % C1-C5 alkanes, 13 - 15 % CO_2, and no O_2 [1]. Under these conditions, solvent degradation is dominated by thermal and CO_2-catalyzed chemical processes. Alkanolamine solvent scrubbing will likely be the technology of choice for CO_2 capture from coal-fired power plants. Flue gas streams would typically be composed of 5 to 7.5 % O_2, in addition to CO_2, SO_2, N_2, and other impurities. The presence of O_2 at these concentrations presents challenges because many alkanolamines such as monoethanolamine (MEA) are susceptible to oxidative degradation. The problem of oxidative degradation of solvents in post-combustion service was addressed by Chakravarti [2] in the development of an approach to strip O_2 from rich amine streams.

We are interested in 7 m MDEA and MDEA blends (7 m MDEA/2 m PZ) because of the history of commercial use of MDEA, and the existence of patents for MDEA promoted with PZ [3]. 7 m MDEA/2 m PZ exhibits a liquid-side mass transfer coefficient (k_g') of 4.5e07 mol/s*Pa*m^2 which is equivalent to the performance of 8 m PZ, and better than 7 m MEA (k_g'~3.1e07 mol/s*Pa*m^2) at comparable rich CO_2 partial pressures [4]. The cyclic capacity of the blend is approximately 0.75 mol CO_2/(kg amine + water) at rich and lean CO_2 partial pressures of 7 kPa and 0.7 kPa, respectively, making this solvent competitive with 7

* Corresponding author. Tel.: +1-512-471-7230; fax: +1-512-471-7060.
E-mail address: gtr@che.utexas.edu.

doi:10.1016/j.egypro.2011.01.018

m MEA and 8 m PZ. Versions of this solvent are already in commercial use for acid gas treatment, and its performance benefits make it attractive as an alternative to MEA for CO_2 capture.

Recent degradation studies have used batch reactors to accelerate oxidative degradation [5], and sealed stainless steel cylinders [6] and microcalorimeters [7] for the rapid screening of solvents for thermal degradation. Those degradation methods generally isolate oxidative or thermal degradation behavior. We degraded solvents in the Integrated Solvent Degradation Apparatus (ISDA), which alternately exposes solvents to oxidative and thermal degradation conditions in a single system. The ISDA simulates conditions observed in an absorber/stripper configuration designed for CO_2 capture. Because these conditions are integrated into a single experimental apparatus, secondary effects have been observed. The ISDA also allows us to evaluate the effect on degradation rates of carryover of dissolved and entrained oxygen into the cross-exchanger and stripper where temperatures can exceed 120 °C.

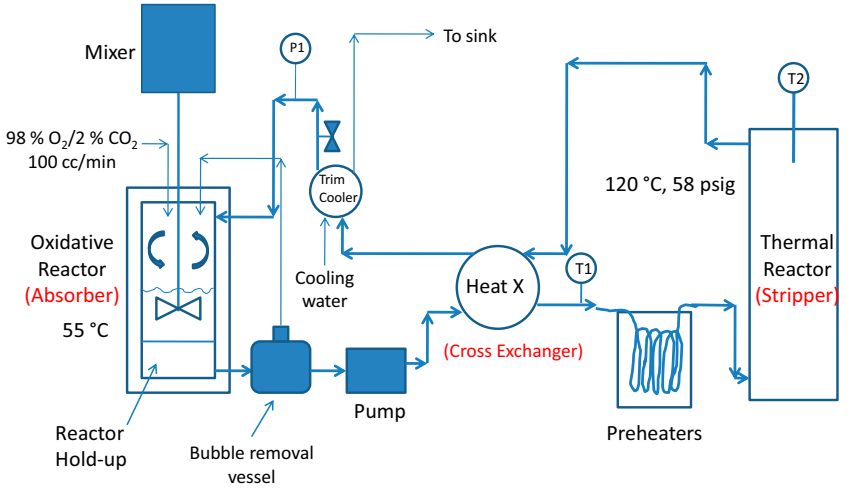

Figure 1 The Integrated Solvent Degradation Apparatus (ISDA)

2. Experimental Methods

The oxidative reactor in the ISDA (Figure 1) is a 750-ml flow-through jacketed glass vessel with an actively stirred top section of 400-ml nominal volume, and a 330-ml bottom section which simulates the sump in an absorber. The top section, which is exposed to a selected gas composition, is agitated at 1,440 rpm to maximize oxygen mass transfer. A 100 cc/min purge gas is introduced to the top section, which typically consists of 98% O_2/2% CO_2. The composition of this gas is varied to study oxidative effects on cycled solvent. Temperature control of the oxidative reactor at 55 °C is achieved by passing water through the jacket-side of the oxidative reactor. The system operates at a nominal liquid flow rate of 200 ml/min, which provides a residence time of 3.5-4.0 minutes in the oxidative reactor.

CO_2-loaded amine is continuously pumped from the bottom section of the oxidative reactor, through a bubble removal vessel, through a positive displacement pump, and into the shell side of a counter-currently operated single-pass tube-in-tube cross-exchanger where it takes on heat from amine exiting the thermal reactor. The amine is then passed through two pre-heaters consisting of stainless steel coiled tubing immersed in oil baths, and enters the internal section of a thermal reactor, which is a 1.2-L stainless steel tube-in-tube heat exchanger. Dimethyl silicone oil is passed through the jacket side of the thermal reactor to heat the amine. The hot amine exits the thermal reactor and passes back through the tube side of the cross-exchanger where it heats the cold amine passing on the shell side. The amine is then passed through a trim cooler (heat exchanger) where it is cooled before passing through a back-pressure valve (¼-inch metering valve) and returning to the oxidative reactor above the liquid surface at atmospheric pressure. All tubing is ¼-inch outer diameter. Materials of construction include 316 stainless steel for tubing, compression fittings, cross-exchanger, and thermal reactor, and glass for the oxidative reactor.

Degraded solvents are analyzed using cation chromatography for amines and degradation products exhibiting amine functionality (alkalinity), anion chromatography for heat stable salts (anions), liquid chromatography with electrochemical detection for amino acids, HPLC coupled to mass spectrometry (MS) and gas chromatography (GC) coupled to MS for identification of polar and non-polar degradation products. Alkalinity is measured using acid titration.

3. Results and Discussion

Figure 2 illustrates degradation product concentrations when 7 m MDEA was cycled from 55 °C in the oxidative reactor to 120 °C in the thermal reactor with a purge gas of 98 % air/2 % CO_2. The primary products identified and quantified in the degraded solvent included diethanolamine (DEA), bicine (bis-hydroxyethylglycine), formate, and formamide, all typical of cycled MDEA. The longer term trends demonstrated by this data indicate a possible competition between MDEA and its products for oxygen in the solvent. Using final concentrations of these products measured with ion chromatography, we

accounted for >55 % of the carbon loss (as MDEA). The carbon associated with DEA comprised >40 % of the carbon in MDEA loss. Table 1 lists MDEA and alkalinity loss and degradation product formation in relevant experiments conducted in the ISDA.

3.1. Temperature Effects/Oxidative Model

The concentration of formate measured in 7 m MDEA when cycled from 55 °C to a series of thermal reactor temperatures (55 to 120 °C) in separate experiments generally increased proportionally with the temperature maintained in the thermal reactor (Figure 3). The rates of formate production listed in Table 1 range from 0.004 mM/hr at 55 °C to 0.31 mM/hr at 120 °C. Very little formate was produced until the thermal reactor was set at 90 °C. However, the change in formate production from a thermal reactor temperature of 100 to 120 °C indicates that, at temperatures above 100 °C, the dissolved oxygen in the solvent may be completely consumed, creating an upper limit to the formate production rate (0.31 mM/hr).

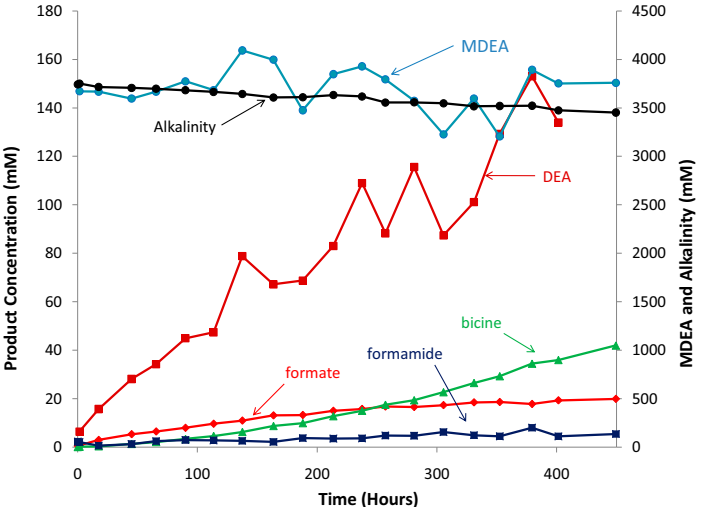

Figure 2 Degradation products in cycled 7 m MDEA

An oxidative degradation model based on degradation product formation in 7 m MDEA was developed to allow prediction of rates of oxidative degradation that can be expected in the heat exchanger and piping entering the top of the steam stripper. These are the most likely locations for oxygen to be present at higher temperatures in a practical absorber/stripper. A simple rate law relationship using the Arrhenius equation over-predicts oxidation rates at temperatures above 100 °C due to complete consumption of dissolved oxygen in ISDA in the thermal reactor.

The basis for the model is that solvent degradation in the ISDA behaves according to isothermal PFR behavior, and that all oxidative degradation occurs in the thermal reactor at the higher experimental temperatures. Rates of degradation product formation over the temperature range 55 to 80 °C are relatively low when compared to 90 °C and above, indicating that oxidative degradation processes are negligible in solvent while passing through the absorber (oxidative reactor in the ISDA). The factor (S) (Equation 1) relates the amount of degradation product formed to the amount of oxygen consumed per pass of solvent through the system. Henry's Law was used to relate dissolved oxygen in the solvent to that in the gas phase in contact with the solvent in the oxidative reactor. The PFR oxidative model (Equation 2) corrects for the depletion of dissolved oxygen at the higher temperatures.

Using degradation product formation rates measured over the thermal reactor temperature range of 55 to 120 °C, we regressed values of activation energy (E_a), rate constant (k_o), and S for formate, bicine and DEA. As a starting point, we chose the measured values of k_o at 90 °C for all components based on the knowledge that dissolved oxygen was not completely consumed at this temperature in the ISDA. We estimated k_o, E_a and S for the three components as listed in Table 2. The model currently provides values of each parameter within an expected range for DEA and formate, but does not provide expected values for bicine. Further, k_o for bicine is three orders of magnitude lower than for DEA, and five orders of magnitude lower than for formate, reflecting the greater tendency for MDEA to degrade to DEA and formate than to bicine. The activation energies (E_a) for DEA and bicine regressed to 85 kJ/mol, and the activation energy for formate regressed to 107 kJ/mol.

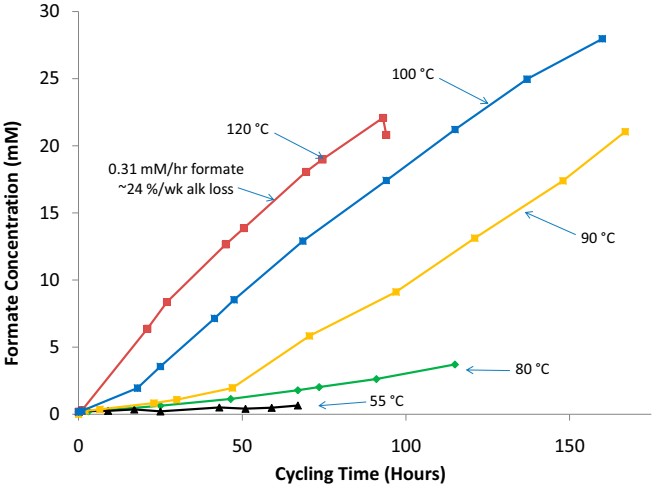

Figure 3 Formate measured with oxidative reactor at 55 °C and thermal reactor varied from 55 to 120 °C

Table 1 - Cycling Experiment Results (7 m MDEA)

Expt	T_{th} (°C)	Stir Rate (rpm)	Purge Gas	Alk Loss (mM/hr)	MDEA Loss (mM/hr)	DEA Prod Rate (mM/hr)	Formate Prod (mM/hr)	Formate w/ Hydrolysis (mM/hr)	Bicine (mM/hr)
C-8	120	1440	N_2/CO_2	1.7	1.9	0	0.013	0.001	0
C-9	120	0	N_2/CO_2	3	4.1	0	0.024	0.002	0
C-13	120	1440	Air/CO_2	0.76	0.24	0.37	0.084	0.08	0.061
C-14	90	1440	Air/CO_2	0.76	0.22	0.08	0.044	0.058	0.062
C-18	120	1440	O_2/CO_2	0.74	0	0.39	0.047	0.044	0.088
C-4	120	520	O_2/CO_2	2.8	3.4	NM	0.17	0.15	NM
C-5	120	1000	O_2/CO_2	4.3	8.5	NM	0.37	0.57	NM
C-1	120	1440	O_2/CO_2	5.2	8.8	NM	0.59	0.98	0.48
C-2	55	1440	O_2/CO_2	1.4	~0.0	NM	0.0052	~0	~0
C-15	90	1440	O_2/CO_2	1.82	2.37	~0	0.15	0.23	0.27
C-7*	120	1440	O_2/CO_2	5.4	5	1.8	0.22	0.29	0.35
C-3	55	1440	O_2/CO_2	1.5	0.9	0	0.0018	0.01	0.05
C-11	80	1440	O_2/CO_2	1.3	0.91	0	0.034	0.057	0.11
C-12	90	1440	O_2/CO_2	2.5	2.87	1.55	0.12	0.15	0.13
C-10	100	1440	O_2/CO_2	3	4.1	1.64	0.18	0.31	0.22
C-6	120	1440	O_2/CO_2	5.3	4.6	2.56	0.31	0.34	0.34

$$S = \frac{\Delta[\mathrm{Pr}]}{\Delta[O_2]} \tag{1}$$

$$\Delta[\mathrm{Pr}] = S * P_{O_2} * Q * t * \frac{1 - e^{-\left(\frac{k * V_{TR}}{Q}\right)}}{H_{O_2} * V_{total}} \tag{2}$$

Figure 4 presents the measured and predicted product formation rates vs. 1/T (K) for the components formate and bicine based on the regressed values of E_a and k_o. The predicted product formation rates approximately match the measured rates over the entire temperature range for formate, with only a slight under-prediction in the middle of the range (80 to 90 °C). For bicine, the match is poor at all but the highest temperatures, which is expected based on the regressed value for S (~4,900). In general, the model provides a better fit for formate than was provided by using a simple rate-law model by compensation for the complete consumption of dissolved oxygen at the higher temperatures in ISDA. The failure of the model to accurately predict formation rates for bicine may also be a result of bicine forming as a degradation product of something other than MDEA in a secondary reaction.

The amount of DEA produced per pass in the system is estimated as 0.7 mM when cycled from 55 to 120 °C, whereas the amount of MDEA degraded was estimated at 1.3 mM per pass. Using dissolved oxygen solubility in water data [8] at 60 °C, we determined that approximately 0.57 mM dissolved oxygen is available, implying a stoichiometric ratio between oxygen available and MDEA consumed per pass of ~0.5. Assuming that all of the MDEA loss was associated with oxidative degradation, the 1.3 mM per pass represents an upper limit of amount of dissolved oxygen available to degrade MDEA.

Table 2 - Regressed Oxidative Model Values

Parameter	Degradation Product		
	Formate	DEA	Bicine
k_o (1/hr)	2.42	0.06	3.388E-05
E_a (J/mol)	107000	85054	85010
S	0.1	16.7	4848.2

3.2. Bubble Entrainment

Based on visual observations of entrained (undissolved) bubbles in solvent exiting the oxidative reactor in early experiments, we sequentially reduced the stir rate in this reactor and observed proportional reductions in formate production (Figure 5). We then installed a bubble removal vessel immediately downstream of the oxidative reactor with 0.24-inch stainless steel unstructured packing to coalesce small entrained bubbles into larger bubbles which could easily escape the solvent before being pumped to the heat exchanger. The formate production rate (0.31 mM/hr) measured with entrained bubble removal (C-6) at full stir rate (1440 rpm) demonstrated that oxidative degradation became dependent primarily on dissolved oxygen, a process governed by the solubility limit of oxygen in solvent at the conditions prevalent in the oxidative reactor (55 °C). All subsequent experiments were conducted with the bubble removal vessel installed in the ISDA. The practical implication of this finding is

that full-scale absorber/stripper systems will need to be designed to minimize the entrainment of dissolved gases as solvent is passed out of the absorber unit. System leaks to the surrounding atmosphere will need to be eliminated to ensure that air is not introduced to the solvent.

3.3. Dissolved Oxygen

In experiments C-8 and C-9, we replaced the 98 % O_2/2 % CO_2 purge gas in the headspace of the oxidative reactor with 98 % N_2/2 % CO_2 gas at 100 cc/min in order to understand the role of thermal degradation in MDEA in the ISDA in the absence of accelerated oxidative degradation. With the exception of the purge gas, all conditions in C-8 were similar to those in C-6. Comparison of experimental results reveals that the alkalinity and MDEA loss were cut in half or better, but the rates of formate and bicine production were reduced by an order of magnitude. No DEA production was observed in experiment C-8 with the 98 % N_2/2 % CO_2 purge gas. These results indicate that DEA is primarily formed through an oxidative degradation process, as evidenced by a production rate of 2.56 mM/hr in experiment C-6.

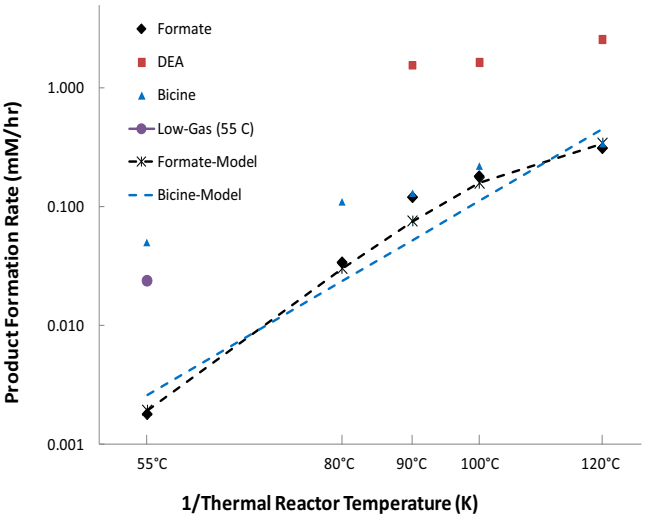

Figure 4 Measured vs. modeled formate rates in cycled 7 m MDEA

In a further effort to understand the role of dissolved oxygen in causing oxidative degradation, and how easily this process could be minimized, a modified bubble removal vessel was constructed of an 8-inch tall (1.25-inch diameter) glass bottle fitted with a fritted stone sparge tube inserted in the lid and reaching the bottom of the vessel. A 2 L/min N_2 gas purge was introduced to the solvent as it passed through this vessel to strip dissolved oxygen from the solvent before being pumped to the cross-exchanger. All other conditions of the experiment were held the same as in previous experiments, including the use of 98 % O_2/2 % CO_2 purge gas in the headspace of the oxidative reactor and a thermal reactor temperature of 120 °C.

The formate production rate (Figure 6) was reduced to 0.05 from 0.31 mM/hr, whereas the MDEA loss rate was reduced from 4.6 mM/hr to a negligible rate, indicating that the oxidation rate was reduced to a rate comparable to that expected when the thermal reactor (stripper) was operated at 80 °C or less. The results of this experiment reaffirm our ability to implement stripping to remove dissolved oxygen and reduce oxidative degradation in alkanolamine solvents.

3.4. Oxidation Inhibitor

Experiments C-7 and C-15 were conducted at conditions similar to C-6 and C-12 (120 and 90 °C, respectively, in the thermal reactor) with the exception that 100 mM of Inhibitor A was added to the solvent. At 120 °C (C-7), the bicine production rate listed in Table 1 was comparable to the rate observed in experiment C-6, indicating that the inhibitor was not effective in the cycling system. At 90 °C, the bicine production rate slightly increased with the inhibitor. The formate production rates are included in Figure 6 and indicate that Inhibitor A had little or no effect at 90 or 120 °C. In general, the data confirm that the inhibitor was ineffective at reducing the rate of oxidative degradation in solvents cycled at these conditions.

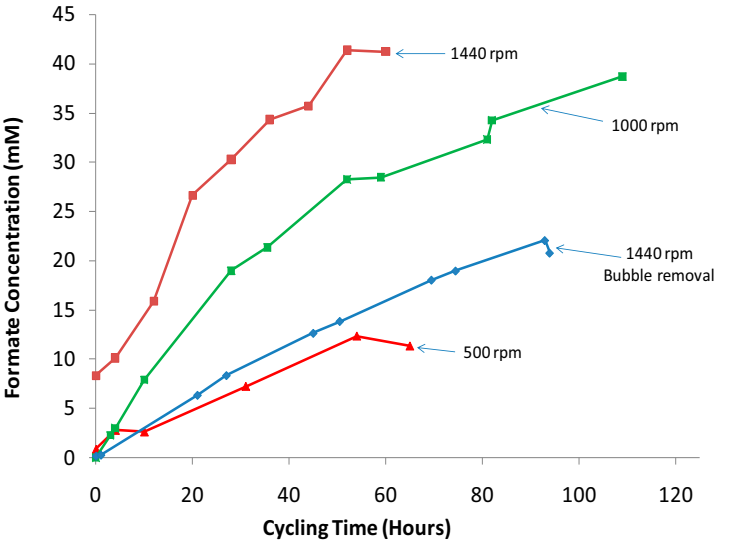

Figure 5 Formate measured in 7 m MDEA cycled from 55 to 120 °C

4. Conclusions

The primary degradation products identified in aqueous 7 m MDEA loaded to 0.1 mol CO_2/mol alkalinity and degraded in the ISDA were DEA, bicine and formate. DEA and bicine represented 43 and 9 % of carbon loss, respectively, after the solvent was cycled for 167 hours.

The rate of MDEA loss was measured as 8.8 mM/hr when 7 m MDEA was cycled from 55 to 120 °C in ISDA in the initial design, which allowed bubble entrainment. When entrained bubbles were removed from the solvent, the loss rate was approximately cut in half (4.6 mM/hr), and the formate production rate was reduced to 0.31 mM/hr. When dissolved oxygen was stripped from cycled MDEA with N_2 gas at 2 L/min, the MDEA loss rate was below detection, and the formate production rate was reduced to 0.05 mM/hr. The MDEA loss rates and degradation product formation rates measured in solvent cycled in ISDA highlight the need for designers of commercial CO_2 scrubbing systems in flue gas post-combustion applications to address dissolved and entrained oxygen accelerating oxidative degradation of aqueous amine solvents. Entrained and dissolved oxygen removal through stripping before amines enter the steam stripping unit (regenerator) is recommended to avoid high temperature oxidation.

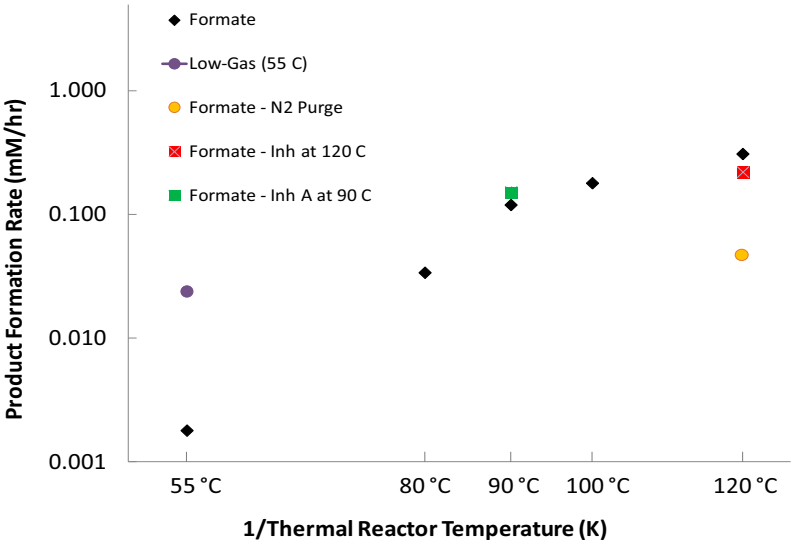

Figure 6 Formate production with/without 100 mM Inhibitor A in cycled 7 m MDEA

An oxygen solubility limit exists at a thermal reactor temperature of 120 °C which can be expressed as an apparent upper limit of dissolved O_2 available to degrade ~1.3 mM MDEA/pass. A simple rate-law model for oxidative degradation over-predicts product formation rates above 100 °C due to accelerated oxidative degradation and an apparent dissolved oxygen solubility limit. We developed an oxidative degradation model which compensates for the complete consumption of dissolved oxygen in the thermal reactor at higher temperatures. The model assumes that all oxidative degradation is occurring in the thermal reactor following PFR behavior. We compensated for complete oxygen consumption with a factor (S) which correlates moles of degradation product produced per moles of oxygen consumed. We regressed values of S, E_a, and k_o for formate of 0.1, 107 kJ/mol, and 2.4 1/hr, respectively. The predicted rates of formate production approximately match the measured rates over the entire measured temperature range of 55 to 120 °C.

When 7 m MDEA cycled from 55 to 120 °C with 98 % N_2/2 % CO_2 as the purge gas, the measured MDEA loss rate was 2 to 4 mM/hr, compared to 4.5 mM/hr when the purge gas was 98 % O_2/2 % CO_2, indicating that, in the absence of oxygen, thermal degradation is causing solvent and alkalinity loss.

When 7 m MDEA cycled from 55 to 90 and 120 °C with 100 mM Inhibitor A, the additive was ineffective at reducing the rate of oxidative degradation, as evidenced by similar formate, bicine and DEA rates measured without the inhibitor with all other conditions held the same.

5. References

[1] Astarita, Gianni and D. Savage and A. Bisio, Gas Treating With Chemical Solvents, J. Wiley & Sons, New York, 1983.
[2] Chakravarti, Shrikar and Amitabh Gupta, "Carbon Dioxide Recovery Plant", Patent Appl. No. 09/774,031, filed January 31, 2001.
[3] Appl, Max and U. Wagner, and H. Henrici, and K. Kuessner, and K. Volkamer, and E. Fuerst, "Removal of CO_2 and/or H_2S and/or COS from Gases Containing these Constituents", Patent Appl. No. 177,615, filed August 13, 1980.
[4] Rochelle, Gary T., Oral Presentation to IUPAC International Meeting, Glasgow, Scotland, August 2009.
[5] Sexton, Andrew, "Amine Oxidation in CO2 Capture Processes", PhD. Dissertation, The University of Texas at Austin, January 2008.
[6] Freeman, Stephanie and J. Davis, and G. T. Rochelle, "Degradation of aqueous piperazine in carbon dioxide capture". International Journal of Greenhouse Gas Control. In print 2010.
[7] Bedell, S. and C.M. Worley, G.Z. Padilla, and A.L. Day, "Methyldiethanolamine (MDEA) Oxidation in Flue Gas CO_2 Capture", presentation paper for SOGAT 4th International CO_2 Forum, Abu Dhabi, April 1, 2010.
[8] Baranenko, V.I., and L.N. Fal'kovskii and V.S. Kirov and L.N. Kurnyk and A.N. Musienko and A.I. Pionkovskii, "Solubility of Oxygen and Carbon Dioxide in Water", Atomnaya Energiya, Vol. 68, No. 4, pp. 291-294, April 1990.